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The space groups of point group C_3: some corrections, some comments

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A survey of the October 2001 release of the Cambridge Structural Database [Cambridge Structural Database (1992). Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England] has uncovered approximately 675 separate apparently reliable entries under space groups $P3$, $P3_1$, $P3_2$ and $R3$; in approximately 100 of these entries, the space-group assignment appears to be incorrect. Other features of these space groups are also discussed.

1. Introduction

This paper represents a survey of the crystal structures described in any of the four space groups of point symmetry C_3 (space-group numbers 143–146) and included in the October 2001 release of the Cambridge Structural Database (CSD; Cambridge Structural Database, 1992). These space groups were selected for two reasons: (i) they constitute a relatively small number of entries in the CSD, approximately 800, so a careful survey seemed feasible; (ii) it seemed likely that this point group might be particularly susceptible to an incorrect interpretation of the structure, because of possible confusion involving the five Laue groups consistent with a hexagonal lattice. It has turned out that nearly 15% of these structures should almost certainly be described in higher symmetries. A few other features of these space groups are also noted.

2. Experimental

Identification of possible candidates for space-group revision was by personal inspection of the coordinates and other crystallographic data available in the CSD; if the entry seemed suspicious, the original article was consulted. Symmetrizing and averaging the coordinates according to the new space group, including an evaluation of the quality of fit to the revised symmetry (Herbstein & Marsh, 1998), involved simple Fortran routines. As is almost invariably the case, the quality of fit, *i.e.* the r.m.s. amount by which the coordinates needed to be shifted, for examples in which only the Laue symmetry was revised was approximately the same as (or, perhaps, slightly smaller than) the coordinate s.u. values reported in the original investigation. However, for examples in which a center of inversion needed to be added, the quality of fit was far worse; coordinate shifts of 0.1 Å or more were not unusual, reflecting the near-singularities present during refinement in the original non-centrosymmetric space group. In these latter cases, the revised interatomic distances and angles are almost always much more reasonable than those originally reported. In two, and only two, cases (NATWAG and NATWEG; see

below) I obtained the original intensity data and carried out satisfactory refinements in the revised space group.

In checking whether an incorrect space group has already been corrected by other authors, it was assumed that the revised structure would be included in the CSD under the same Refcode but with a different extension. There is some danger here, as identical compounds occasionally appear under different Refcodes, and it is possible that a corrected structure was overlooked. I apologize for any oversights that may have resulted. Revised coordinates have been submitted to the CSD.[1]

Table 1
Structures originally described in space group $P3$ that are properly described in higher symmetries.

Included are the reference codes (Refcodes) assigned by the Cambridge Structural Database (1992), the revised space group, the number of formula units per cell (Z) and the formula unit.

Refcode	Space group	Z	Formula unit	Reference
CIGLIN	$P312$	1	$C_{77}H_{69}N_3O_2P_6Pd_2Co\cdot PF_6$	Bachert *et al.* (1999)
HILVIH†‡	$P6_3/m$	2	$C_{18}H_{60}P_3Al_3Si_6$	Janik *et al.* (1998)
HONNAZ	$P6_3/m$	2	$C_{16}H_{29}N_3O_6$	Feichtinger *et al.* (1998)
QATZEQ	$P\bar{3}$	1	$3(C_{12}H_{24}S_6Fe)\cdot 2(C_6N_6Fe)\cdot 2(H_2O)$	Pavlishchuk *et al.* (2001)
SENYIT§	$P\bar{3}$	2	$C_{21}H_{24}SiGe$	Pannell *et al.* (1990)
VEHHAR	$P\bar{3}$	18	$C_3H_{17}B_{11}N\cdot C_4H_{12}N$	Novák *et al.* (1990)
WEWHIP§	$P\bar{3}$	2	$C_{27}H_{22}BN_6In$	Frazer *et al.* (1994)
ZIRNAP§	$R\bar{3}$	18	$C_{21}H_{19}N_3O$	Verardo *et al.* (1995)
ZOMROI¶	$P321$	2	$C_{40}H_{108}Si_{12}Te_4In_4\cdot 1.5(C_6H_{12})$	Uhl *et al.* (1996)

† Space group given as $P\bar{3}$ in original paper. ‡ In the same paper, the structure of the related compound $C_9H_{29}NSi_2AlAs$, HILVON, should be corrected from space group $P2_1$ to $Cmc2_1$. Revised coordinates are included in the supplementary material. § The original space-group assignment of $P3$ apparently resulted from a misprint. The coordinates are correct. ¶ See text.

3. Results

3.1. Space group $P3$

$P3$ (number 143) is not a popular space group: it is represented by only 83 entries in the October 2001 release of the CSD, describing approximately 55 separate, apparently reliable, structures. In four cases – Refcodes DETTUR (Marsh, 1987), LAKRIY and LAKROE (Marsh *et al.*, 2002), and LOHSOQ (see text) – the space group has already been revised; in another case, the original authors could not decide whether $P3$ or $P6$ was more appropriate and included coordinates from refinements in both (GIKDOT and GIKDOT01). There appear to be nine additional examples for which the space group should be revised to one of higher symmetry. These are listed in Table 1.

Three of the compounds listed in Table 1 represent cases where an error in space-group designation was apparently due only to a misprint – the lack of the 'overline' in the symbol $P\bar{3}$, as noted previously for many examples in space group $P1$ (Marsh, 1999). (In the case of ZIRNAP, a second misprint – P for R – must also be present.) In all three cases, entirely reasonable intermolecular contacts result if space group $P\bar{3}$ (or $R\bar{3}$) is used without revising the coordinates in any way; in addition, the number of formula units in the cell becomes reasonable.

The entry LOHSOQ – a fullerene complex with bis(triphenylphosphinechlorogold) (Spitsina *et al.*, 2000) – warrants special comment. The coordinates given for the three independent fullerene molecules and the six independent Au complexes in space group $P3$ can be matched across a common center of inversion within r.m.s. deviations of about 0.05 Å (much less for the Au, Cl and P atoms), a typical value for such near-centrosymmeteric cases. However, the quality of matching is almost exactly the same when the resulting centrosymmetric units are matched according to rhombohedral lattice centering, so as to create space group $R\bar{3}$; such a matching would also involve near-singularities in the refinement process because of the superlattice situation (Schomaker & Marsh, 1979). Balch, Maitra & Olmstead (LOHSOQ02; private communication to the CSD) have carried out an independent investigation of this structure based on data collected at 140 K. (Data for LOHSOQ were collected at room temperature.) They report the space group as $R\bar{3}$, and their coordinates are in good agreement with those obtained by symmetrizing the $P3$ coordinates of LOHSOQ according to $R\bar{3}$. Apparently the original authors of LOHSOQ (Spitsina *et al.*, 2000) collected intensity data appropriate for a primitive hexagonal lattice and concluded (or were told by their computer) that reflections that would be absent if the lattice were rhombohedrally-centered, *i.e.* those with $(-h + k + l) \neq 3n$, were sufficiently strong to require a primitive lattice. These additional reflections might also have biased statistical tests so as to suggest a non-centrosymmetric structure. Another example of a structure that was originally reported in space group $P3$ but later revised to rhombohedral is DETTUR. In that case, new experimental data (Marsh, 1987) showed the true space group to be $R32$ (DETTUR01), with the apparent violations to the rhombohedral centering condition being due to scan overlap from neighboring allowed reflections. The original data had been collected on a serial diffractometer, as was the case for LOHSOQ.

The compound listed under ZOMROI is reported by the authors (Uhl *et al.*, 1996) to contain toluene of crystallization, since the material was crystallized (from cyclopentane) starting with a 'toluene-containing solid'. However, the two independent toluene molecules were reported as sixfold disordered, and the methyl groups were not apparent; the coordinates correspond, within 0.1 Å, to planar aromatic six-membered rings such as benzene. In the CSD, the solvent is reported as hexane, with formula C_6H_{12}. The situation is, indeed, confusing.

3.2. Space groups $P3_1$ and $P3_2$

There are 369 entries under these two space groups (numbers 144 and 145), representing approximately 320 separate seemingly reliable structures. One entry (TANROP)

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0117). Services for accessing these data are described at the back of the journal.

Table 2
Structures originally described in space group $P3_1$ or $P3_2$ that are more properly described in higher symmetries.

Refcode	Space group	Z	Formula unit	Reference
APLYSU01	$P3_121$	6	$C_{15}H_{21}O_3Br$	Capon *et al.* (1981)
BECXEM	$P3_221$	3	$C_{32}H_{46}O_8S$	Lam & Martin (1981)
BIHZEX†	$P3_121$	3	$C_{18}H_{16}N_2O_8CuNi{\cdot}H_2O$	Morgenstern-Badarau *et al.* (1982)
BIHZIB†	$P3_221$	3	$C_{18}H_{16}N_2O_8Ni_2{\cdot}H_2O$	Morgenstern-Badarau *et al.* (1982)
CACSOO	$P3_121$	3	$C_{22}H_{28}Fe_2$	Jonas *et al.* (1983)
COHQEV	$P3_121$	6	$C_{13}H_{24}O_3$	Lochýnski *et al.* (1999)
DCAZPD	$P3_121$	3	$C_{24}H_{20}N_4Cl_2Pd$	Khare *et al.* (1975)
DUWFUW	$P3_121$	3	$C_{20}H_{38}ClPS$	Boese *et al.* (1986)
FEKQIV	$P6_2$	3	$C_{34}H_{36}N_4S_3Zn$	Burth & Vahrenkamp (1998)
FIQPOK	$P3_112$	3	$C_{24}H_{16}N_{10}S_2Pd{\cdot}3H_2O$	Liu *et al.* (1999*a*)
GESTIH‡	$P3_121$	3	$C_{15}H_{45}O_8S_4P_5Pd_5{\cdot}C_6H_6$	Bott *et al.* (1988)
GOTLOQ	$P3_212$	3	$C_{24}H_{16}N_{10}S_2Pt{\cdot}3H_2O$	Liu *et al.* (1999*b*)
HELMOA	$P3_221$	3	$C_2H_3N_2P$	Polborn *et al.* (1999)
HELPOD	$P3_221$	3	$C_2H_3N_2As$	Polborn *et al.* (1999)
HINVOP	$P6_4$	3	$C_{14}H_{14}N_2O_4W$	Wong *et al.* (1999)
JOGPAW§	$P3_121$	3	$C_{34}H_{48}N_2O_2Co$	Sakiyama *et al.* (1991)
KIHBIM¶	$P3_221$	3	$C_5H_{13}N_2B$	Schmid *et al.* (1990)
LOMZES	$P3_112$	3	$C_{15}H_{34}N_6Br_4Zn_2$	DasGupta *et al.* (2000)
LOVPER	$P3_221$	3	$C_{52}H_{54}O_{10}F_{12}P_2Rh_2{\cdot}2H_2O$	Lahuerta *et al.* (2000)
NAVVAH	$P3_121$	3	$C_{32}H_{40}O_8F_{12}NaEr$	Polyanskaya *et al.* (1997)
NIPMAA	$P3_212$	3	$C_6H_6N_4Ag{\cdot}NO_3$	Hester *et al.* (1997)
NODLUN	$P3_221$	3	$C_{34}H_{54}N_2Si_4Ni_2$	Rosenthal *et al.* (1998)
PERBAP	$P3_121$	3	$C_{57}H_{44}O_7P_2S_2Mo_2{\cdot}C_4H_8O$	Sellmann *et al.* (1993)
PIQWIV	$P3_121$	3	$C_{35}H_{33}N_4O_{11}S_2Fe_2{\cdot}NH_4$	de Brito *et al.* (1997)
RUHJAF	$P3_221$	3	$C_{17}H_{24}N_4O_3$	Schreiner & Pruckner (1997)
RULVAV††	$P3_112$	3	$C_{48}H_{94}N_8O_{31}Cl_3Mn_3{\cdot}6H_2O$	Yano *et al.* (1997)
SOTROI	$P3_221$	3	$C_{10}H_7N_2O_{10}CuCr_2$	Klüfers & Wilhelm (1991)
TAXZOH	$P3_121$	3	$C_{20}H_{22}N_4O_2$	Mazik *et al.* (1996)
TUJFUZ	$P3_221$	3	$C_{216}H_{180}Se_{50}Hg_{32}$	Behrens*et al.* (1996)
WEKKEC	$P3_221$	9	$C_{22}H_{28}O_2P_2IV$	Gailus *et al.* (1994)
WIXJIW	$P3_221$	3	$C_{56}H_{40}N_4O_8Zn_2{\cdot}H_2O$	Evans *et al.* (1999)
XAXJOV	$P3_221$	3	$C_{36}H_{42}N_2O_6Fe_2Pd_2{\cdot}CH_2Cl$	Zhao*et al.* (1999)
XEJYOA	$P3_112$	3	$C_{48}H_{94}N_8O_{31}Mn_3Br_3{\cdot}8H_2O$	Tanase *et al.* (2000)
XEVTEX	$P6_4$	3	$C_{18}H_{16}N_2O_5Cl_2$	Ochoa *et al.* (2001)
YASROZ	$P3_12121$	3	$C_{10}H_{14}N_2O_8Co{\cdot}H_4O_{1.5}$	Horn *et al.* (1993)
YONLIW‡‡	$P3_221$	6	$C_{29}H_{44}O_9{\cdot}0.5(C_3H_6O)$	Höfle *et al.* (1995)
ZARSEQ	$P6_4$	3	$C_{32}H_{42}N_2P_2Si_2$	Weller *et al.* (1995)
ZEVYOO	$P3_121$	3	$C_{24}H_{38}N_2O_2Os$	Chin *et al.* (1995)
ZIFYOC	$P3_221$	6	$C_{50}H_{46}N_5O_{21}P_4Pr$	Aparna *et al.* (1995)
ZUKKOF	$P3_121$	3	$C_{18}H_{18}N_2O_2$	D'Angeli *et al.* (1996)

† These two compounds are isostructural (but enantiomeric). ‡ There are peculiar bond angles, whatever the space group, apparently because of disorder involving both the trimethylphosphine groups and the benzene solvent molecule. In $P3_121$ a disordered $P(Me)_3$ group lies on a C_2 axis; it was ignored. § JOGPEA, the corresponding Cu compound, is reported as isomorphous. No coordinates are available. ¶ In the same paper, the structure of KIHBOS, $C_5H_{11}BN_2$, should be corrected from $P4_3$ to $P4_32_12$; revised coordinates are included in the supplementary material. Also, the space group of KIHBAE, the low-temperature determination of $C_7H_{17}BN_2$, was misprinted as C_c but is corrected to $C2/c$ in the CSD; the space group of the high-temperature determination (KIHBAE01) should also be revised (no coordinates available). †† In $P3_121$, the two hydrate species lie on twofold axes. They have very large U_{ij}s and their H atoms were not located. ‡‡ No coordinates are available for the disordered acetone.

has already been revised to space group $P3_121$ (TANROP01); 40 additional revisions are reported here. None of these revisions involve adding a center of inversion; the revised structures remain chiral, with higher point symmetry. In all cases, an additional C_2 axis has been added, usually along the [100] or [110] direction but occasionally along [001] so as to create hexagonal symmetry. The revisions are listed in Table 2.

Of special note is the entry BIHZEX (and, by implication, the related compound BIHZIB). This compound is a heterobinuclear (Cu and Ni) compound with chelation to a Schiff base; BIHZIB is the corresponding homobinuclear Ni, Ni compound. The authors (Morgenstern-Badarau *et al.*, 1982) noted that X-ray powder spectra 'strongly suggest' that the Cu, Ni compound BIHZEX is isomorphous with the corresponding Cu, Mg compound (Refcode, FSALCM; Beale *et al.*, 1979) and with the Cu, Co compound CUCOES (Mikuriya *et al.*, 1978), which were described in space groups $P3_121$ and $P3_221$, respectively, and hence that the Laue group of BIHZEX might be $\bar{3}m1$; they reportedly ruled out this Laue group by comparing the intensities $I(hkl)$ with $I(\bar{h}kl)$, $I(i\bar{k}l)$, $I(hk\bar{l})$ and $I(khl)$. However, none of these comparisons is relevant to $\bar{3}m1$. They also noted that '...our structure analysis gave a correlation matrix showing clearly that the molecules do not adopt a genuine twofold axis', but unusual correlations are not to be expected in cases involving a change in Laue symmetry (Schomaker & Marsh, 1979). The coordinates for both BIHZEX and BIHZIB are compatible with the higher symmetries within the reported s.u. values of about 0.003 Å for BIHZEX and 0.005 Å for BIHZIB; the U^{ij} values show equivalent agreement. There can be no doubt that BIHZEX, BIHZIB, CUCOES and FSALCM are isostructural (except for enantiomerism) in Laue group $\bar{3}m1$.

3.3. Space group *R*3

There are 362 entries under the space group $R3$ (number 146), representing approximately 300 separate apparently valid structures. Six of these compounds (BOLDIP, CECLIF, CIVCEP10, DETBAA06, FUSWAR and GATMAP01) also appear elsewhere in the CSD with different extensions to the Refcodes, under higher-symmetry space groups, representing corrections or independent investigations; four other entries – JOSTEQ, JUNNAH, TAZPAD and ZATGIK – have recently been revised to higher symmetries (Marsh & Spek, 2001; Marsh *et al.*, 2002) but do not yet appear in the CSD. In one instance, the authors submitted coordinates for separate refinements, based on the same experimental data, in two separate space groups: $R3$ (PYNONI01) and $R\bar{3}$ (PYNONI). While they preferred the $R\bar{3}$ results, they note that 'the statistics favor a non-centrosymmetric distribution'. [It is probable that the misleading statistics were due to the presence of a single relatively heavy atom (Ni) in the primitive unit cell; see Hargreaves (1955).]

We are left with 35 additional examples where the space group should be revised (Table 3). Of the entries in Table 3, 14 are cases in which the space-group error was due to the familiar 'lack-of-overline' misprint situation. (In a few of these instances, the space group $R\bar{3}$ appears correctly in the original

article, so the missing overline presumably occurred in the supplementary material supplied to the CSD.)[2] The remaining entries comprise failures to recognize the presence of a center of inversion, the assignment of an incorrect Laue symmetry or a combination of both. In almost all cases there is no indication, in the original article, that the authors considered the possibility of higher symmetry.

For NATWAG and NATWEG, I was able to obtain listings of the observed structure factors and carried out additional refinements in the revised cubic space group. For both compounds, the final R values, as well as the values of R(merge), were essentially the same as the final R values reported for the $R3$ refinements – 0.07 for NATWAG, 0.03 for NATWEK. Note that the cell dimensions of a related Ga_4S_4 cluster compound ZUWVES (Power *et al.*, 1995), which is also reported in space group $R3$, can similarly be transformed into body-centered cubic; in this case, however, the deviations of the atom coordinates from cubic symmetry seem unacceptably large.

The entry PERRAF deserves comment. Here, every atom either lies on or is paired across the additional C_2 axis of space group $R32$ within 0.02 Å, with the exception of the Bi atom, which lies 0.1 Å from the C_2 axis, a highly significant displacement. It is likely that this displacement is due either to the omission of or, more probably, to the inverted assignment of the anomalous scattering term $\delta f''$ for the Bi atom, resulting in a 'polar dispersion error' as noted by Ueki *et al.* (1966); the amount of the displacement, 0.1 Å, is approximately what would be expected if the $\delta f''$ value for Bi (and Mo radiation – about 10.5 e^-) had been introduced with the incorrect sign (Cruickshank & McDonald, 1967). As a result of this displacement, the two *trans* Bi—N bonds, which are directed approximately along the c direction, appear to be markedly different in length (2.43 Å and 2.71 Å), while the two Bi—Cl and the two Bi—O bonds, which have only small components along c, are approximately equal (in pairs). Intensity data were collected on a four-circle (serial) diffractometer (Hegetschweiler *et al.*, 1993), but there is no indication as to what portion of the reciprocal lattice was surveyed or how the refinement (*SHELXTL-PLUS*88) was carried out.

Table 3
Structures originally described in space group $R3$ that are more properly described in higher symmetries.

Refcode	Space group	Z	Formula unit	Reference
BENRAN	$R32$	3†	$C_{34}H_{32}N_2Nb_2O_2\cdot BF_4\cdot CH_3NO_2$	Lemenovskii *et al.* (1982)
BIVLUN	$R\bar{3}$	9	$C_8H_{20}O_4S_2Si_2$	Balbach *et al.* (1982)
BOSVEK	$R\bar{3}$	54	$C_6H_6O_2\cdot 0.02(SO_2)$	Polyanskaya *et al.* (1982)
CUKGIY	$R3m$	3	$C_{15}H_{21}Ni_3P_3$	Deppisch *et al.* (1984)
DEQMOB	$R\bar{3}$‡	6	$C_{36}H_{43}N_6BPAg$	Santini *et al.* (1998)
DFPECR	$R\bar{3}$‡	2†	$C_{12}H_{15}O_3F_3P_3Cr$	Nesmeyanov *et al.* (1979)
DUXJIP	$R\bar{3}$‡	6	$C_{54}H_{69}B_4N_3$	Männig *et al.* (1986)
FAFKEC	$R\bar{3}$‡	6	$C_{12}H_{18}N_2$	Nelsen *et al.* (1986)
FESBOU	$R32$	3	$C_{12}H_{30}P_3S_6Bi\cdot C_6H_6$	Sowerby & Haiduc (1987)
GEHDUS	$R\bar{3}$‡	6	$C_{48}H_{45}N_3Cu\cdot CF_3SO_3\cdot 0.5(CH_2Cl_2)$	Stamp & Dieck (1988)
GOZYOJ	$R\bar{3}$	6	$C_3H_6O_6Ru\cdot 2(BF_4)$	Funaioli *et al.* (1999)
HOVCAW	$R\bar{3}m$	3	$C_{24}H_{54}N_8$	Kim *et al.* (1999)
HPGEBZ10	$R\bar{3}$	3	$C_{36}H_{30}Ge_2\cdot 2(C_6H_6)$	Dräger & Ross (1980)
JENYUW	$R\bar{3}m$§	6	$C_{15}H_9O_9Os_3Rh$	Colombie *et al.* (1990)
JIHZAB	$R32$	3	$C_{12}H_{12}N_2O_{12}Bi\cdot 3(NH_4)$	Suiarov *et al.* (1990)
JOMGEX	$R\bar{3}$	3	$CHB_{11}Br_{11}\cdot Cs$	Xie *et al.* (1998)
LIFMUI	$R\bar{3}$‡	3	$C_{20}H_{24}NAl$	Fisher *et al.* (1994)
MEDYOJ	$R\bar{3}$‡	3	$C_{27}H_{39}U$	Conejo *et al.* (1999)
NATWAG	$I\bar{4}3m$¶	2	$C_{28}H_{60}Ga_4S_4$	Gillan *et al.* (1997)
NATWEK	$I\bar{4}3m$¶	2	$C_{28}H_{60}Ga_4Se_4$	Gillan *et al.* (1997)
NINRAD	$R\bar{3}$‡	6	$C_{17}H_{15}Se_3As$	Baldwin *et al.* (1996)
NUQVAW	$R\bar{3}$¶	9	$C_{16}H_{20}O_6F_6Cu$	Gromilov *et al.* (1997)
PAMKEE	$R3$‡	6†	$C_{18}H_{28}N_6$	Hamodrakas *et al.* (1992)
PERRAF	$R32$¶	3	$C_{12}H_{24}N_6O_6ClBi_3\cdot 2Cl\cdot 6H_2O$	Hegetschweiler *et al.* (1993)
PIMXEO	$R32$	3	$3(C_6H_{24}N_6Cr)\cdot FeCl_6\cdot 6Cl\cdot H_2O$	Moron *et al.* (1994)
PIMXIS	$R32$	3	$3(C_6H_{24}N_6Co)\cdot FeCl_6\cdot 6Cl\cdot H_2O$	Moron *et al.* (1994)
POQRUI	$R\bar{3}$	6	$C_{68}H_{56}N_4P_4Ag\cdot ClO_4$	Del Zotto & Zangrando (1998)
QANPOK	$R32$	3	$C_{27}H_{33}N_3O_{13}Ru_3$	Marr *et al.* (2000)
RACKAH	$R\bar{3}$	3†	$C_{58}H_{64}N_6O_4\cdot C_4H_6N_2O_2$	Adams *et al.* (1996)
RENYIS	$R\bar{3}$‡	6	$C_{62}H_{57}N_{10}OP_3\cdot 2(H_2O)$	Alajarin *et al.* (1997)
RURVOP	$R\bar{3}$‡	6†	$C_{18}H_{12}N_3O_2F_6PS_2$	Vij *et al.* (1997)
SIWXEB	$R\bar{3}$‡	9	$C_{24}H_{36}O_2F_4P_2Cl_4Ru_2$	Bell *et al.* (1991)
VINDAX	$R\bar{3}$‡	6†	$C_{13}H_{10}N_4O_7$	Gridunova *et al.* (1990)
ZAJZIT	$R\bar{3}c$	6	$C_{24}H_{34}P_2F_4BAu\cdot 2(CHCl_3)$	Sladek & Schmidbauer (1995)
ZOBBAT	$R\bar{3}$‡	36	$C_{12}H_{10}NO_2P$	Skvortsev *et al.* (1995)

† Rhombohedral cell. ‡ Misprinted as $R3$; coordinates are correct. § Space group given as $R\bar{3}$ in original paper, $R3$ in CSD. ¶ See text.

4. Discussion

The four space groups discussed here constitute but a small fraction of the entries in the CSD: only 800 or so out of 250000. They were selected for survey because of a preconceived notion that structures in this point group might be particularly susceptible to incorrect interpretation, owing to confusion involving the five Laue groups ($\bar{3}$, $\bar{3}m1$, $\bar{3}1m$, $6/m$ and $6/mmm$) consistent with a hexagonal lattice. Indeed, all but one ($6/mmm$) of these five Laue groups are represented in the lists of revised structures, which also include the cubic group $\bar{4}3m$. Failure to include the 'overline' symbol was responsible for 17 incorrect designations of space groups $P\bar{3}$ and $R\bar{3}$.

No attempt has been made to keep track of the experimental techniques used in these examples of erroneous structures; occasionally such information is not available. In almost all cases the intensity data were obtained from serial diffractometers; structure solutions and refinements usually involved some version of *SHELX*.

As usual, clear distinction must be made between examples in which the revision in space group involves a change in Laue symmetry and those in which the revision involves the addi-

[2] The entry NUQVAW shows other symptoms. The space group is given as $R\bar{3}$ in the original paper, but the coordinates clearly define a nearly centrosymmetric arrangement in $R3$, the space group listed in the CSD.

tion of a center of inversion within the same Laue group. (Entries HONNAZ in Table 1 and HOVCAW and ZAJCIT in Table 3 involve both.) When only a change in Laue symmetry is involved, the changes in molecular geometry should be minimal – no greater than, and probably slightly smaller than, the s.u. values of the derived coordinates (Schomaker & Marsh, 1979). However, when an inversion center must be added, the well known singularity problem leads to far more serious consequences, and apparent bond lengths can be in error by 0.1 Å or more. Moreover, since small deviations from centrosymmetry are effectively impossible to detect by diffraction methods, there cannot be definitive conclusions as to whether a structure is truly centrosymmetric or only approximately so. The decision to choose the centrosymmetric description in all cases described here was made primarily on the basis of the pronounced – spectacular, in many cases – improvement in molecular dimensions that results from symmetrizing the coordinates.

However, in some cases there can be uncertainty in the choice of space group, even where the proper choice should be clearly dictated by the Laue symmetry. Three examples can be cited:

(i) CIDNEI. The structure of this compound, $C_{24}H_{60}N_8O_3^{6+}\cdot 6Br^-$, is described in space group $P3_1$ [Laue group $\bar{3}$; Dietrich *et al.* (1984)]. The deviations from $P3_121$ (Laue group $\bar{3}m1$), while small, appear to be statistically significant; they are concentrated in the atoms around one of the three ether linkages in this cage compound. However, the bond lengths and angles in this region are unsatisfactory, with aliphatic C—C distances of 1.69 Å and 1.95 Å and a C—C—N angle of 82°; the authors suggest that disorder may be responsible. (The final R value was high, at 0.092.) Symmetrizing the structure so as to correspond to $P3_121$ does little to improve the geometry. The structure of the corresponding hexachloride compound, with similar cell dimensions, is reported in $P3_121$, but few details of the experimental methods are given for either compound. The Laue symmetries are not specified.

(ii) TIWREW. The structure of this compound, $C_{16}H_{36}N^+\cdot C_{10}F_{15}^-$, is described in space group $P3_2$ (Chambers *et al.*, 1997); however, as the authors noted, the diffraction symmetry is compatible with Laue group $\bar{3}m1$. The authors attempted refinement in $P3_221$ (which requires that one CF_3 group be disordered about the C_2 axis) as well as in $P3_2$ but had problems with disorder of the entire perfluoropentamethylcyclopentadienyl group in both space groups; they finally opted for the $P3_2$ description. (I have repeated the refinements, based on the original data kindly provided by Dr A. S. Batsanov, and included a model with inversion twinning, with similarly inconclusive results.)

(iii) DAZHOB. This polymeric compound of empirical formula $C_{12}H_8N_2CuCN$ was reported in space group $P3_1$ (Dyason *et al.*, 1985). As the authors note, the coordinates conform very closely to space group $P3_121$; however, the added C_2 axis would require that the C and N atoms of the bridging CN groups be disordered. The authors obtained slightly better refinement in $P3_1$ ($R = 0.041$ *versus* 0.044 in $P3_121$), and note that the resulting $P3_1$ coordinates lead to a Cu—C bond slightly shorter than Cu—N, as expected (1.88 Å *versus* 1.95 Å, a difference of about 3σ.)

In the cases of CIDNEI and TIWREW, there appears to be extensive disorder that prevents an accurate structure analysis, and there seems little reason to fret over the choice of space group. The situation is somewhat different for DAZHOB, where the parallel refinements in $P3_1$ and $P3_121$ seem to favor the former. However, as the authors note, the deviations from $P3_121$ are very small: the r.m.s. deviation from the additional C_2 axis is only marginally larger than the mean coordinate uncertainty. From a chemical standpoint, it would be interesting to confirm (if the $P3_1$ model is correct) that asymmetric bonding of the two cyanide groups linked to each Cu atom – one Cu—C bond and one Cu—N bond in an ordered arrangement in $P3_1$ – has no detectable effect on the remaining coordination about Cu (which apparently retains C_2 symmetry, whichever the space group). The crucial experiment would be a careful evaluation of the symmetry of the measured intensities, to determine if the true point symmetry is 3 or 321. (The authors do not indicate what region of reciprocal space their intensity measurements covered or how – or if – the intensities were averaged. Since the compound contains an anomalous scatterer, Cu, it would have been helpful to collect Friedel mates.)

It is emphasized once again that in cases such as DAZHOB, where the choice between the two space groups is dictated by the symmetry of the diffraction pattern, there is no inherent problem in near-singularity; refinement in the lower-symmetry space group should proceed without incident to yield the correct structure, whichever the space group. (It is the *recognition* of the proper symmetry that occasionally causes problems.) However, there may be some confusion in the selection of an appropriate region of reciprocal space to survey during data-collection time, particularly for trigonal or hexagonal symmetries. For a structure of Laue symmetry $\bar{3}m1$ (as in space group $P3_121$), the region with h, k and l all non-negative, for example, constitutes an asymmetric unit; if the Laue symmetry is $\bar{3}$ (as in $P3_1$), an additional region such as l negative is required for a complete survey. If this additional region is not surveyed, and refinement is carried out in $P3_1$, singularities are not to be feared (unless the number of data is too small).[3] The situation is quite different from the centrosymmetric–non-centrosymmetric ambiguity, where the presence of an approximate center of inversion leads to severe correlations between pairs of pseudo-related atoms, and a highly distorted structure will probably result.

In few other instances did the original authors indicate any ambiguity in their choice of space group. A notable exception is VEHHAR, a carborane cage compound with 18 formula units (including tetramethylammonium counterions) in the cell. Here the authors (Novák *et al.*, 1990) note that intensity statistics suggested 'centricity and even ... hypercentricity'.

[3] In this situation, as in any situation involving an incomplete data set, correlations within the parameter sets of the individual atoms may become important, but interatomic correlations should not be unusual.

However, their attempts to solve the structure in space group $P\bar{3}$ (*MULTAN*80) were unsuccessful, and they apparently failed to realize that the structure they derived in *P*3 is, in fact, closely centrosymmetric. The situation was complicated by the fact that the structure is pseudo-rhombohedral, and, in order to comply with space group $P\bar{3}$, the *P*3 coordinates must be shifted to an alternative C_3 axis as origin.

5. Added comments

With few exceptions, the 83 CSD entries for space group *P*3 represent structures for which the major molecular component lies on a C_3 axis of symmetry; that is, the C_3 axis of the space group is accommodated by molecular C_3 symmetry. It is perhaps even more noteworthy that in well over half of these cases there are three such molecules in the cell, lying on the three distinct C_3 axes of the space group; the three molecules are displaced from one another, along the C_3 axes, by varying amounts so as to form a pseudo-rhombohedral array. For these structures, it is usual that two of the molecules are oriented in one direction (along the C_3 direction) while the third has the opposite orientation. Such an arrangement creates local pseudo screw axes between all pairs of neighboring molecules within the trigonal array; some of these 'screw' axes are oriented parallel to *c* and others parallel to the (*ab*) plane. Screw axes are, of course, far more common crystallographic symmetry elements than pure rotors [see, for example, Brock & Dunitz (1994)]. The use of C_3 axes as elements of molecular symmetry is not quite as apparent in space group *R*3, where it occurs in slightly more than 50% of the entries; here, of course, all three molecules must have the same orientation, and pseudo screw axes parallel to the (*ab*) plane are ruled out. Molecular symmetry is not available in $P3_1$ or $P3_2$, although in a few instances (such as DAZHOB; see above) polymeric helices can be identified. The difference in the number of entries in space group $P3_1$ (206) compared with $P3_2$ (163) presumably is due to their ordering in space-group tables: an investigator who is unable to decide between the two (or is uninterested in the chirality of the compound) will probably select space group number 144 rather than 145. With the exception of PERRAF (see above), no example has been found in any of these four space groups where systematic bond-length differences would suggest polar dispersion errors indicative of incorrect chirality, as might result if $P3_1$ and $P3_2$ had been interchanged by mistake.

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